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CITATION:

Matsubara, Yasuhiko ...[et al]. The transference numbers of KCl aqueous solution under pressure. The Review of Physical Chemistry of Japan 1973, 43(1): 24-32

ISSUE DATE:

1973-09-01

URL:

http://hdl.handle.net/2433/46982

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 43, NO. 1, 1973

THE TRANSFERENCE NUMBERS OF KCL AQUEOUS SOLUTION UNDER PRESSURE

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The transference numbers of K^+ ion in KCl aqueous solutions have been determined at high pressure up to 1,500 kg/cm^2 at the concentration from 0.01 to 0.1 N at 25°C and at 0.02 N at 15 and 40°C by the moving boundary method. The movement of the boundary was detected by the resistance measurement. Cadmium chloride was used as an indicator solution. The transference numbers at infinite dilution at 25°C were calculated by the empirical equation of Longsworth. The K^+ ion transference numbers decrease with the increase in pressure in all cases. This decreasing tendency becomes weaker with the increase in temperature. Besides, the K^+ ion transference number increases slightly with the increase in temperature at 1500 kg/cm^2, while it decreases with the increase in temperature at atmospheric pressure. The ion-water interaction of K^+ ion is mostly dominated by the electrostriction, while the ion-water interaction of Cl^- ion involves the hydrogen bond additionally. It is considered that the hydrogen bond in the hydration shell of Cl^- ion is broken with the increase in pressure and/or temperature as that in pure water. That is to say, the hydration of Cl^- ion decreases to a small degree with the increase in pressure and/or temperature.

Introduction

Accurate data on the limiting equivalent conductances Λ° of electrolytes at infinite dilution give valuable information for the understanding of ion-solvent interaction. From this point of view, in our laboratory, the effects of temperature and pressure on the electrical conductances of electrolytes in aqueous solutions have been studied. When we want to discuss the cation- and anion-water interactions, we need to know the ionic transference numbers of electrolytes. Unfortunately, in spite of numerous accurate measurements of the conductances of aqueous solutions under high pressure, only a few measurements of the transference numbers were reported[1~4]. Then, the transference numbers of K^+ ion in KCl aqueous solutions were determined precisely under high pressures up to 1,500 kg/cm^2. From the data obtained, the pressure and temperature effects on the transport processes of K^+ and Cl^- ions and, especially, on their ion-water interactions are discussed in this paper.

(*Received April 13, 1973*)

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1) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, 59, 278 (1955)
2) F. T. Wall and J. B. Berkowitz, *ibid.*, 62, 87 (1958)
3) R. L. Kay, K. S. Pribadi and B. Watson, *ibid.*, 74, 2724 (1970)
4) G. J. Hills, P. J. Ovenden and D. R. Whitehouse, *Discussions Faraday Soc.*, 39, 207 (1965)

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Experimental

Method

There are several methods available for measuring the transference numbers at atmospheric pressure: the Hittorf method, the moving boundary method, the electromotive force method, the analytical boundary method, *etc.* The moving boundary method[1~3] and the electromotive force method[4] have been adopted to the studies under pressure.

In the case of the moving boundary method, the movement of the boundary is observed by the optical method utilizing the difference in the refractive index between the two solutions, or by the measurement of the change in the electrical resistance of the column of the solutions. The former is more desirable at atmospheric pressure because the direct observation of the displacement of the boundary is possible. But it is not the case at high pressure. For the high pressure measurement, the latter is much more convenient because of the simplicity and the precision of measurement. This electrical method has been adopted at high pressure first by Wall and Gill[1]. The appropriateness of this method has been discussed in comparison with the optical method at atmospheric pressure by Lorimer, Graham and Gordon[5]. Thus, this electrical method was chosen for measuring the transference numbers at high pressure.

Now, let two electrolytic solutions having a common anion form a boundary in a long tube of uniform cross-section A cm^2, and let constant current i mA pass through the column of the solutions so that the boundary of the solutions may move up. The transference number t_+ can be calculated from the equation[6],

$$t_+=\frac{cAFx}{is}, \tag{1}$$

when the boundary moves up at a distance of x cm for s seconds, where F is the Faraday constant and c the concentration of the observed solution in equiv/l.

Two probe electrodes are built in the cell in which the boundary moves upward. The boundary is set initially in the region below the lower of these probe electrodes. If the specific resistances of the leading and the following solutions are different, the resistance R of the solution between the probe electrodes will change with the moving up of the boundary. And the change has a linear relation to the displacement of the boundary by Ohm's law when the current i is constant and the cross-section A is uniform between the probe electrodes. Then the resistance R is given by

$$R=R_1+\frac{x}{l}(R_2-R_1), \tag{2}$$

where l is the distance between the probe electrodes in cm, R_1 the resistance when the boundary is in the region beneath the lower probe electrode and R_2 the resistance when the boundary in the region above the upper probe electrode. Provided the displacement of the boundary is Δx while the current

5) J. W. Lorimer, J. R. Graham and A. R. Gordon, *J. Am. Chem. Soc.*, **79**, 2347 (1957)
6) D. A. MacInnes and L. G. Longsworth, *Chem. Rev.*, **11**, 171 (1932)

has been passed for a time Δs, the change of the resistance ΔR is given by

$$\Delta R=\frac{\Delta x}{l}(R_2-R_1). \tag{3}$$

The transference number t_+ is given by combining Eqs. (1) and (3) as follows:

$$t_+=\frac{cFA}{i\Delta s}\cdot\frac{\Delta Rl}{(R_2-R_1)},$$

$$=\frac{cFAl}{i(R_2-R_1)}\cdot\frac{\Delta R}{\Delta s}. \tag{4}$$

Apparatus and Procedure

The high pressure transference number cell made of glass, platinum, teflon and the adhesive, Araldite, is shown in Fig. 1. The oil pressure in the pressure vessel is transmitted to the solution by the glass piston (G) of the syringe. The cadmium anode (B) was carefully fitted at the lower end of the capillary tube of the cell which was sealed with the DeKhotinsky cement (A). The silver-silver chloride cathode (E) was made by dipping a platinum wire into molten AgCl and allowing the AgCl to solidify upon the platinum wire. The probe electrodes (D) for the measurement of the resistance of the solution were made of platinum wire, being lightly coated with platinum black to avoid polarization. The distance between these probe electrodes is about 6.5 cm. The internal diameter of the capillary tube is about 2 mm.

First the KCl aqueous solution was put into the cell without bubbles. When the direct current was passed between the cadmium anode and silver-silver chloride cathode, the $CdCl_2$ solution was

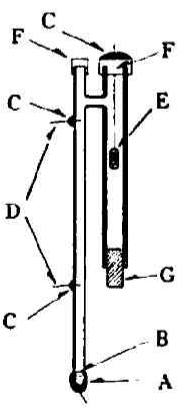

Fig. 1 The high pressure transference number cell
A: DeKhotinsky cement
B: Cadmium anode
C: Araldite
D: Probe electrode
E: Silver-silver chloride cathode
F: Teflon capsule
G: Glass piston

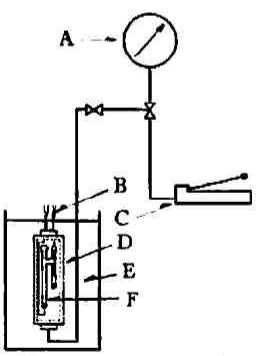

Fig. 2 The pressure generating layout
A: Bourdon type pressure gauge
B: Leading wire
C: Hand pump
D: High pressure vessel
E: Paraffin oil bath
F: High pressure transference number cell

formed at the metal surface of cadmium anode by electrolysis and the boundary generated autogenically between the KCl and $CdCl_2$ solutions moved up in the direction of the current flow. The pressure generating layout is shown in Fig. 2. The Heise gauge of the Bourdon type was calibrated with a free piston gauge. The pressure produced in the pressure vessel was kept constant within $\pm 0.3\%$. The temperature in the pressure vessel was kept constant in a constant temperature oil bath regulated within ± 0.05°C. For the constant current operation, the direct current stabilizer, Metronics 691 A type, was used. The current was measured with a Shimadzu digital potentiometer in conjunction with a 120 Ω standard resistor. The resistance between the probe electrodes was measured with the Yanagimoto MY 7 type a. c. bridge. While a resistance measurement is made by using the probe electrodes, the direct current for electrolysis should be stopped for one minute. It has been known from the studies by MacInnes and Longsworth[6] that interruptions of the current produce no detectable effect on the observed transference numbers. In the present experiment, their conclusions were confirmed again.

The parameters A and l peculiar to the cell used are to be known so as to obtain the transference numbers according to Eq. (4). The product $A \cdot l$ is the effective volume between the probe electrodes and determined at atmospheric pressure on the basis of the transference numbers of K^+ ion in KCl aqueous solutions according to Allgood, Roy and Gordon[7]. The transference number of K^+ ion in 0.02 N KCl aqueous solution at 40°C was interpolated from their data. The product $A \cdot l$ under pressure depends upon the compressibility of the material of the cell. The product $A \cdot l$ at high pressure was corrected with the compressibility of Pyrex glass at 25°C[8]. The change of the product $A \cdot l$ with temperature was calculated, assuming that the thermal expansibility is equal to 8.5×10^{-6}[9] at all the pressures. The concentrations of the dilute solutions at high pressure were corrected with the volume of water at the corresponding pressure and temperature calculated by the Tait equation[10],

$$\frac{V(1)-V(P)}{V(P)}=C \log \frac{B+P}{B+1}, \qquad (5)$$

where B and C were the characteristic parameters of water. Also, the volume corrections by electrode reactions and the solvent conductance corrections were not made since they both should be negligible.

Results and Discussions

The variations of the resistance for a typical run is shown in Fig. 3.

The observed transference numbers of K^+ ion in KCl aqueous solutions at 25°C are shown in Table 1 and compared with other data[2,3] at 0.02 N in Fig. 4. The agreement is very satisfactory.

7) R. W. Allgood, D. J. Le Roy and A. R. Gordon, *J. Chem. Phys.*, 8, 418 (1940)
8) L. H Adams, *J. Am. Chem. Soc.*, 53, 3769 (1931)
9) "Kagaku Binran" (Hand Book of Chemistry), ed. ited by the Chemical Society of Japan, Maruzen (1958)
10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Chap. 5, Reinhold, New York (1958)

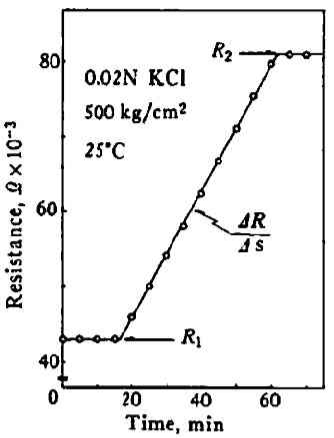

Fig. 3 Typical plots of resistance against time

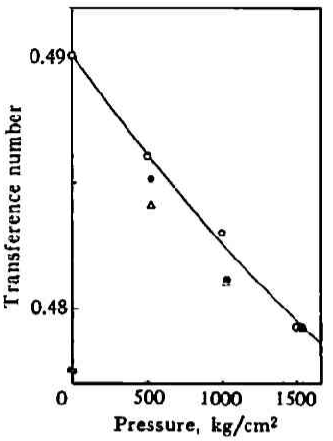

Fig. 4 Variation of the transference number of K^+ ion in 0.02 N KCl aqueous solution at 25°C with pressure
○: This work
△: Wall and Berkowitz[2]
●: Kay, Pribadi and Watson[3]

Table 1 The transference numbers of K^+ ion, t_+, in KCl aqueous solutions at 25°C under pressure

Pressure	Concentration at 1 atm, N			
	0.01	0.02	0.05	0.1
1 atm	0.4902	0.4901	0.4900	0.4900
500 kg/cm²	0.4865	0.4861	0.4858	0.4856
1,000 kg/cm²	0.4835	0.4830	0.4833	0.4814
1,500 kg/cm²	0.4817	0.4793	0.4803	0.4803

For many 1–1 electrolytes at 25°C at atmospheric pressure, Longsworth[11] showed that t_+' is linear against the concentration C as follows,

$$t_+' = \frac{t_+ \Lambda' + 1/2 B_2 \sqrt{C}}{\Lambda' + B_2 \sqrt{C}} = t_+^\circ + AC, \tag{6}$$

where

$$\Lambda' = \Lambda^\circ - (B_1 \Lambda^\circ + B_2)\sqrt{C}, \tag{7}$$

$$B_1 = \frac{8.204 \times 10^{-5}}{(DT)^{3/2}}, \tag{8}$$

and

$$B_2 = \frac{82.50}{(DT)^{1/2}\eta^\circ}, \tag{9}$$

where t_+° is the transference number at infinite dilution, A a constant, t_+ the transference number at concentration C, Λ° the equivalent conductance at infinite dilution, D the dielectric constant of the solvent and η° the viscosity of the solvent. We assumed that this empirical equation was applicable

11) L. G. Longsworth, *J. Am. Chem. Soc.*, 54, 2741 (1932)

under high pressure. The value of D[10], η°[12] and Λ°[13] at 25°C under pressure are cited as shown in Table 2. Fig. 5 shows the results of t_+' at four pressures. The values of t_+° obtained from the intercept of the slope of t_+' against C are summerized in Table 3 and shown in Fig. 6.

Table 2 D, η° and Λ° (KCl) at 25°C under pressure

Pressure	D	η°, c.p.	Λ°, $\Omega^{-1}\cdot cm^2\cdot equiv^{-1}$
1 atm	78.36	0.8903	149.9
500 kg/cm²	80.51	0.8865	152.5
1,000 kg/cm²	82.47	0.8897	153.4
1,500 kg/cm²	84.29	0.9034	152.9

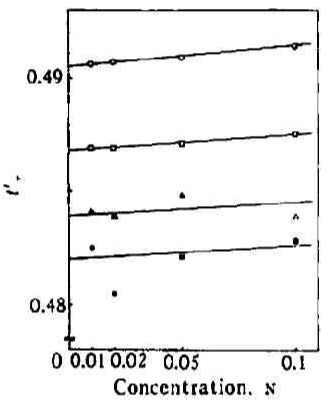

Fig. 5 Plots of t_+' against concentration
○: 1 atm
□: 500 kg/cm²
△: 1000 kg/cm²
●: 1500 kg/cm²

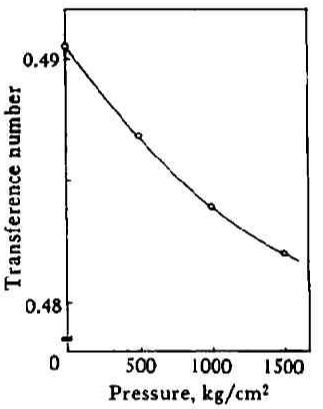

Fig. 6 Variation of the transference number of K^+ ion in KCl aqueous solution at infinite dilution at 25°C with pressure

Table 3 $t^\circ_+(K^+)$, $\lambda^\circ(K^+)$, $\lambda^\circ(Cl^-)$, $\lambda^\circ(K^+)\eta^\circ$ and $\lambda^\circ(Cl^-)\eta^\circ$ at 25°C under pressure

Pressure	$t^\circ_+(K^+)$	λ°, $\Omega^{-1}\cdot cm^2\cdot equiv^{-1}$ K^+	Cl^-	$\lambda^\circ\eta^\circ$ (×10) K^+	Cl^-
1 atm	0.4905	73.5	76.4	6.55	6.80
500 kg/cm²	0.4868	74.2	78.3	6.58	6.94
1,000 kg/cm²	0.4839	74.2	79.2	6.60	7.05
1,500 kg/cm²	0.4820	73.7	79.2	6.66	7.15

The equivalent conductances of K^+ ion and Cl^- ion at infinite dilution, $\lambda^\circ(K^+)$ and $\lambda^\circ(Cl^-)$, are calculated from the combination of the transference numbers t_+° of K^+ ion with the equivalent conductances at infinite dilution Λ° of KCl aqueous solution. These results at 25°C under pressure are given in Table 3 and shown in Fig. 7 in comparison with the results by Hills, Ovenden and White-

12) J. B. Cappi, Ph. D. Thesis, London University (1964)
13) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)

house[4] who measured the equivalent conductances at infinite dilution of HCl aqueous solution and the transference numbers at infinite dilution of H^+ ion in HCl aqueous solution by the electromotive force method under pressure up to 2,000atm. Both the results for the limiting conductance of Cl^- ion under pressure agree qualitatively.

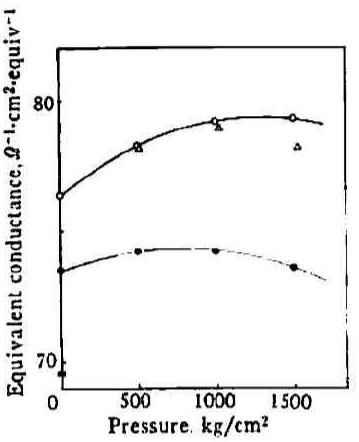

Fig. 7 $\lambda^\circ(K^+)$, and $\lambda^\circ(Cl^-)$ at 25°C under pressure
●: $\lambda^\circ(K^+)$
○: $\lambda^\circ(Cl^-)$
△: $\lambda^\circ(Cl^-)$, Hills, Ovenden and Whitehouse[4]

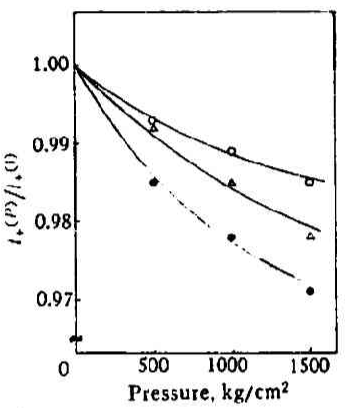

Fig. 8 The transference number ratio $t_+^{(P)}/t_+^{(1)}$ at various temperatures
●: 15°C
△: 25°C
○: 40°C

The equivalent conductance of K^+ ion at infinite dilution at 25°C has a maximum at a pressure between 500 and 1,000 kg/cm² and then decreases at higher pressure. On the other hand, Cl^- ion has a greater equivalent conductance at infinite dilution and a greater pressure coefficient than K^+ ion at 1 atm. And the equivalent conductance of Cl^- ion increases with the increase in pressure up to 1,500 kg/cm². This pressure effect is made clear by the comparison of the pressure dependency of the Walden products $\lambda^\circ\eta^\circ$ between K^+ ion and Cl^- ion. These values are given in Table 3. The Walden products of these ions increase with the increase in pressure, but the pressure dependency of the Walden product of Cl^- ion is much greater than that of K^+ ion. As the modified Stokes law[14,15] expresses the Walden product by the equation,

$$\lambda^\circ\eta^\circ = \frac{|z|eF}{6\pi r_e}, \tag{10}$$

the increasing of Walden product with the increase in pressure can be explained qualitatively by the

14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Chap. 6, Butterworths, London (1965)
15) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), 92, 785 (1971)
16) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)
17) E. Inada, K. Shimizu and J. Osugi, *This ibid.* 42, 1 (1972)

compression of the effective radius r_e of the hydrated ion[13,16,17]. However, it is difficult to explain such great difference of the pressure dependency of the Walden product between K^+ ion and Cl^- ion merely by the compression of the effective radii, because the hydration shell of the former is thicker than that of the latter[15]. Therefore, it should be considered that there is substantial difference in the ion-water interaction between K^+ ion and Cl^- ion as described later.

The transference numbers of K^+ ion in 0.02 N at the temperature of 15, 25 and 40°C under high pressures are shown in Table 4. As shown in Table 1, the transference numbers of K^+ ion in KCl

Table 4 The transference numbers of K^+ ion, t_+, in 0.02 N KCl aqueous solution under pressure

Pressure	Temperature, °C		
	15	25	40
1 atm	0.4924	0.4901	0.4876
500 kg/cm²	0.4849	0.4861	0.4841
1,000 kg/cm²	0.4815	0.4830	0.4822
1,500 kg/cm²	0.4783	0.4793	0.4802

aqueous solutions at 25°C scarcely change with the concentration. It would not be unreasonable to expect the same tendency at any other temperature to discuss the general profile of the transference numbers of K^+ ion by using the data of the finite concentration in Table 4 instead of those at infinite dilution. The ratio of the transference number of K^+ ion in 0.02 N KCl aqueous solution under high pressure to that at atmospheric pressure $t_+^{(P)}/t_+^{(1)}$ is plotted against pressure at various temperatures in Fig. 8. Fig. 8 shows that the transference numbers of K^+ ion decrease with the increase in pressure and its tendency becomes weaker with the increase in temperature. This result indicates that the higher the temperature is, the smaller the difference in the ion-water interaction between K^+ ion and Cl^- ion is.

The ion-water interaction of K^+ ion is mostly dominated by the electrostriction, while the ion-water interaction of Cl^- ion involves the hydrogen bond additionally[15]. It is considered that the hydrogen bond in the hydration shell of Cl^- ion is broken down with the increase in pressure and/or temperature as that in water. That is to say, the hydration of Cl^- ion decreases to a small degree with the increase in pressure and/or temperature[18].

In Table 4 the transference number of K^+ ion decreases with the increase in temperature at atmospheric pressure but increases slightly at 1,500kg/cm². At atmospheric pressure the breaking effect of temperature on the hydrogen bond in the hydration shell of Cl^- ion is appreciable, while at higher pressure this temperature effect is not appreciable because of the breaking effect of pressure on the

18) M. Nakahara, *This Journal*, 42, 75 (1972)
19) R. L. Kay and G. A. Vidulich, *J. Phys, Chem.*, 74, 2718 (1970)
20) M. Born, *Z. Physik.*, 1, 221 (1920); R. M. Fuoss, *Proc. Natl. Acad. Sci. (U. S.)*, 45, 807 (1959); R. H. Boyd, *J. Chem. Phys.*, 35, 1281 (1961); R. Zwanzig, *ibid.*, 38, 1603 (1963), *ibid.*, 52, 3625 (1970)

hydrogen bond in the hydration shell of Cl^- ion. And the increasing in the transference number of K^+ ion with the increase in temperature at 1,500 kg/cm^2 consists with the tendency[19] expected by the model on a moving ion which was proposed by Born, Fuoss, Boyd and Zwanzig[20].

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